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A Method for Manufacturing Polyester for Use in Highly Heat-Resistant Polyester Bottles

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(54) [Title of the Invention]:

**A Method for Manufacturing Polyester for Use in Highly Heat-
Resistant Polyester Bottles**

Abstract

The invention relates to a method for manufacturing a polyester resin (PET, polyethylene terephthalate) suitable for the manufacture of polyester bottles with outstanding heat resistance that can be filled with high-temperature beverages, characterized in that, using purified terephthalic acid (TPA) and ethylene glycol (EG) as the main raw materials, catalysts, cocatalysts, and thermal stabilizers are mixed in appropriate concentrations to manufacture a base chip having intrinsic viscosity (IV) in the range of 0.55 to 0.67 dL/g, and the chip is then crystallized and subjected to solid-state polymerization to obtain a heat-resistant resin showing high viscosity of 0.70 to 1.0 dL/g.

The highly heat-resistant resin of the invention can be used for the molding of high-transparency bottles having particularly outstanding characteristics with respect to heat deformation, crystallization, and shrinkage during high-temperature filling of fruit beverage bottles with liquids ranging from 85 to 105°C.

In particular, the invention provides a polyester resin that can be molded into a high-transparency bottle that can be used for the filling of beverages in a temperature range of 90 to 95°C, considerably higher than the range for conventional heat-resistant bottles (filling temperature 85 to 88°C).

Specification

Detailed Description of the Invention

Purpose of the Invention

Technological Field of the Invention and Prior Art

The invention relates to a method for manufacturing a polyester resin suitable for the manufacture of polyester bottles with outstanding heat resistance that can be filled with high-temperature beverages.

Initially, PET (polyethylene terephthalate) was used mainly in the field of textiles as a thermoplastic polyester resin manufactured by reacting purified terephthalic acid (TPA) and dimethyl terephthalate (DMT) with ethylene glycol (EG), but it is currently used in the molding of biaxially-oriented stretch-blown bottles, which are widely used in applications such as containers for bottled water, carbonated beverages, alcoholic beverages, fruit juice drinks, and wrapping of general food products.

In particular, PET containers show outstanding mechanical properties, gas barrier properties, chemical resistance, transparency, and luster, and their use is expected to increase considerably in the future.

The majority of PET containers are used for filling of contents at room temperature or temperatures of 70°C and above, while filling of fruit juice beverages is carried out at temperatures of 85 to 88°C. High-temperature filling is carried out in order to meet the requirements of sterilization, bleaching, and prevention of oxidation.

When molded containers made of such existing PET resins are sterilized by hot-water washing, they tend to undergo deformation, so it has been difficult to use them as containers for high-temperature sterile filling.

Technical Problems to be Solved by the Invention

In manufacturing the polyester resin (PET) of the invention, which has a highly transparent, high-viscosity, highly heat-resistant linear polymer structure, by selecting and mixing the additives to be used at the melt polymerization stage, one can optimize the manufacturing conditions for clean polymers and the molding conditions for heat-resistant bottles, thus providing a method for manufacturing a polyester resin and molding bottles made of said resin that makes it possible to produce highly heat-resistant containers in which the beverage filling temperature can be increased from the existing level of 85 to 88°C to a level of 92 to 100°C.

In the polyester manufacturing method of the invention, terephthalic acid and dimethyl terephthalate (DMT) are mixed with ethylene glycol and subjected to polyester polymerization in order to obtain a polyester resin having a linear polymer structure, thus obtaining a highly heat-resistant polyester resin that makes it possible to keep the container shrinkage ratio at 1.5 or less during high-temperature liquid filling at temperatures of 90°C or above.

The bottle molding method according to the invention makes it possible to manufacture PET resin having the physical properties of intrinsic viscosity of 0.5 to 1.0 and a melting point of 245 to 260°C. By means of a process in which the preform is molded at a temperature of 275 to 295°C, crystallization of the neck portion is carried out at 100 to 200°C, heat-setting is carried out at 160 to 200°C, and multistage blowing is carried out at a temperature of 90 to 120°C and a pressure of 20 to 40 kg/cm², one obtains a container suitable for the filling of high-temperature liquids at 90°C or above.

Composition and Operation of the Invention

The following is a detailed explanation of the polyester resin manufacturing method and bottle molding method of the invention.

In the invention, high-purity terephthalic acid (TPA) and ethylene glycol (EG) are used as raw materials, and catalysts, thermal stabilizers, cocatalysts, color-improving agents, etc., are mixed in at specified concentrations to obtain a base polymer having an intrinsic viscosity (IV) of 0.550 to 0.670 dL/g, after which crystallization and solid-state polymerization are carried out to manufacture a high-viscosity resin having an intrinsic viscosity (IV) of 0.70 to 1.0 dL/g, thus providing a process for molding bottles used for the filling of high-temperature beverages.

PET is prepared as a base polymer having a degree of polymerization of approximately 100 by carrying out esterification and polycondensation using terephthalic acid (TPA) and

ethylene glycol as the main raw materials, and this base polymer is then subjected to crystallization and solid-state polymerization in order to obtain a high-viscosity polymer (having an intrinsic viscosity of 0.70 to 1.0 dL/g).

Substances such as high-purity isophthalic acid, phthalic acid, 1,4-cyclohexane dimethanol, diethylene glycol, and bisphenol derivatives may be used as the main raw materials.

Important physical properties of the resin include intrinsic viscosity (IV), color, melting point, carboxy end groups, diethylene glycol (DEG) content, etc.

Concerning pellet size, in order to make the degree of crystallization and the melting point uniform after polymerization, it is preferable to manufacture the base polymer under as sterile conditions as possible beginning from the manufacturing stage, with pellets ordinarily being manufactured in a weight range of 1.5 to 3.0 g per 100 pellets.

As problems such as non-uniform physical properties or unstable material flow may occur during the solid-state polymerization process when pellets are made in excessively small powder form in order to increase their relative surface area, the particular characteristics of the equipment used should also be borne in mind.

Antimony trioxide and antimony triacetate are used as polymerization catalysts, with a mixing ratio of the two substances of 0 : 1,000 to 50 : 50, and the catalyst used must be high-purity catalyst (purity of 99.80%) virtually free of insoluble impurities such as Sb_nO_m ($n = 2$, $m = 3$ to 5) and metallic components such as Pb and N.

Moreover, in order to impart thermal stability during postprocessing, phosphorus compounds may be mixed in and used together with ethylene glycol in manufacturing, and in order to improve resin color, cobalt acetate and tin compounds may be used in specified concentrations as cocatalysts.

Catalysts, cocatalysts, heat stabilizers, etc., may be added immediately before esterification or polycondensation, completely dissolving and dispersing them in the ethylene glycol, after which precision filtering is carried out using a 1 to 2 μ filter.

In particular, in order to achieve a uniform melting point and stabilize molecular structure, it is extremely important to maintain a uniform concentration and a stable quantitative supply of such submaterials.

Antimony trioxide, antimony triacetate, and germanium oxide may be used as polycondensation catalysts either alone or in combination in concentrations of 200 to 750 ppm/PET, phosphorus compounds may be used as thermal stabilizers in concentrations of 100 to 200 ppm/PET, and cobalt acetate in a concentration of 50 to 200 ppm and tin compounds in a concentration of 10 to 100 ppm may be used as cocatalysts. Phosphates such as trimethyl phosphate, triethyl phosphate, and triphenyl phosphate may be used as phosphorus compounds.

In the esterification stage, the reaction is carried out at a pressure of approximately 1.0 kg/cm^2 and a temperature in the range of 245 to 260°C to obtain an oligomer having a degree of polymerization of 3 to 10, after which, in the polycondensation stage, the reaction is carried out at 275 to 285°C under a high vacuum with a pressure of 1 torr or less to manufacture a melt polymer with an intrinsic viscosity of 0.57 to 0.67 dL/g and a standard pellet weight of 1.5 to 3.0 g/100 pellets.

The basic pellets, which have a super bright, fully transparent linear polymer structure, are subjected to the various phases of precrystallization, crystallization, and solid-state polymerization in order to manufacture a high-viscosity resin having a degree of crystallization of 45 to 60 and an intrinsic viscosity of 0.70 to 1.0 dL/g .

This solid-state resin has a melting point ranging from 245 to 260°C , and it is therefore used not only as a material for bottles filled with high-temperature beverages but also in ordinary pressurized and non-pressurized containers.

PET has a glass transition temperature (T_g) of 67 to 81°C , and the temperature at which deformation begins to occur is approximately 70°C . It has been confirmed that if high heat resistance is imparted from the resin manufacturing stage and appropriate heat setting is carried out in the container molding process, it is possible to manufacture stable, heat-resistant PET containers for hot filling with beverages at much higher temperatures than the range of 85 to 88°C possible with conventional containers.

This heat-resistant PET resin is manufactured with an intrinsic viscosity of 0.70 to 1.10 dL/g , it is then dried to reduce its water content to 50 ppm, and it is molded into a bottle using the molding machine described below. The bottle-molding method of the invention is described in the following.

1. Drying of PET pellets

The pellets are dried for 3 to 6 hours at a temperature of 140 to 180°C so as to reduce their water content to 50 ppm or below.

2. Molding of preform

The preform is molded at 270 to 295°C .

3. Crystallization of neck component

The neck component is crystallized by cooling from a temperature of 100 to 125°C for 200 to 400 sec with water chilled to a temperature of 10 to 30°C .

4. Heat setting and blowing

Primary blowing is first carried out at 15 to 30 kg/cm^2 and 80 to 140°C .

The heat-setting temperature is set at 160 to 190°C .

Secondary blowing is carried out at 20 to 45 kg/cm^2 and 80 to 130°C .

5. Testing and packaging

External appearance and transparency tests, heat resistance tests (testing of shrinkage 5 minutes after filling with hot water at 92°C).

In order to mold a high-temperature beverage container from pellets obtained by high-viscosity solid-state polymerization, the pellets must be dried to a water content of 50 ppm or less. The preform is manufactured under injection molder barrel temperature conditions of 270 to 295°C, after which the mouth portion of the preform (bottle mouth) is crystallized at 100 to 125°C, cooled, and then sent to the blowing unit.

The mouth of the bottle is crystallized because it is the first part to come into contact with the high-temperature beverage during filling. In the process of molding the mouth component, the crystallized preform is heated in the blowing device to 80 to 140°C and subjected to primary blowing with compressed air at a pressure of 50 to 30 kg/cm², after which the temperature is increased to 160 to 190°C, heat setting is carried out, and secondary blowing is carried out using compressed air at a temperature of 80 to 130°C and a pressure of 20 to 45 kg/cm², thus manufacturing the completed molded form into a heat-resistant bottle.

During the testing process, testing of the external appearance of the bottle is carried out, including properties such as heat resistance, uniformity of drawing, specimen thickness, and bottom gate center properties, and in order to measure heat resistance, the bottle is filled with hot water at a temperature of approximately 92°C and left standing for a period of 5 min. or longer, the volume before and after filling with hot water is measured, and the shrinkage rate is determined.

Although there are differences among the standards used at various bottle manufacturing companies, a tolerance has been adopted of a change in shrinkage rate of 1.5 or less in testing with hot water at 92°C.

[Working Examples]

Antimony acetate in the amount of 500 to 700 ppm/PET, cobalt acetate in the amount of 100 to 150 ppm/PET, triethyl phosphate in the amount of 150 to 200 ppm, and a tin compound in the amount of 10 to 50 ppm were added to high-purity terephthalic acid (TPA) and ethylene glycol (EG) to manufacture a resin (polymer), which was then subjected to solid-state polymerization up to an intrinsic viscosity of 0.85 to manufacture a 1.5 L juice container.

Table 1. Physical properties of melt polymer (base polymer) and solid-state polymer

Classification	Intrinsic viscosity (IV)	Color		Carboxyl end group (Eq/TON)	Melting point (°C)	Acetaldehyde (ppm)	DEG content (wt)	100EA weight (g)	Bottle shrinkage after molding (%)
		L	b						
Base polymer	0.654	51.2	-0.46	18.6	255.8	55.0	1.21	2.5	0.6
Solid-state polymer	0.851	89.0	2.3	2.3	252.8	0.30	1.15	2.5	

* The melt polymer was manufactured by batch polymerization, and the solid-state polymer was manufactured using a continuous-type unit.

Table 2. Molding conditions of heat-resistant bottle

Molding step		Production conditions		
Pellet drying		160°C x 4 h		
Injection molder barrel temperature (preform manufacturing)	Neck	Front		Rear
		280°C	280°C	280°C
Crystallization of neck component		110°C x 300 sec		
Primary blowing		25 kg/cm ² x 170°C		
Heat setting		180°C x 6 sec		
Secondary blowing		350 kg/cm ² x (100-104°C)		
Chilled water		15°C Chilled Water		
Molded bottle	Volume		1.5 L Juice bottle	
		Transparency	Haze 0.3 or below (favorable)	
			Favorable	
			Shrinkage 0.6 (92°C hot water)	

As shown in Tables 1 and 2 above, by molding a heat-resistant bottle using resin manufactured by the method of the invention, it was possible to obtain a bottle allowing filling of a beverage at 92 to 100°C, a much higher temperature than bottles currently on the market, and hot-water-induced shrinkage was also confirmed to be outstanding, with a value of 1.

Effect of the Invention

In contrast to conventional molded fruit drink bottles, which ordinarily can be filled with hot beverages at temperatures of 85 to 88°C, the invention provides a polyester resin that allows manufacturing of a heat-resistant bottle that has raw materials with improved internal density, allows filling temperatures over a broad range, does not show deformation at temperatures of 90 to 95°C, and shows a broad range of thermal resistance over a range of 85 to 100°C.

(57) Claims

Claim 1

A method for manufacturing a polyester resin having a linear polymer structure by polyester polymerization of dimethyl terephthalic acid and dimethyl terephthalate (DMT) with ethylene glycol, characterized in that said polyester resin can be used to manufacture heat-resistant bottles that allow filling of high-temperature liquids at temperatures of 90°C or above and show container volume shrinkage of 1.5 or less.

Claim 2

The method for manufacturing a polyester resin for use in heat-resistant containers according to Claim 1,

characterized in that antimony trioxide, antimony triacetate, or germanium oxide are added alone or in combination in amounts of 200 to 750 ppm/PET as polycondensation catalysts, a phosphorus compound is added in the amount of 100 to 200 ppm/PET as a heat stabilizer, and cobalt acetate in the amount of 50 to 200 ppm or a tin compound in the amount of 10 to 100 ppm are added as cocatalysts.

Claim 3

The method for manufacturing a polyester resin according to Claim 2,
characterized in that the above phosphorus compound is trimethyl phosphate, triethyl phosphate, or triphenyl phosphate.

Claim 4

The method for manufacturing a polyester resin for use in a heat-resistant fruit juice beverage container according to Claims 1 or 2,

characterized in that high-purity isophthalate, phthalic acid, 1,4-cyclohexane dimethanol, diethylene glycol, or bisphenyl derivatives are used as additives.

Claim 5

The method for manufacturing a container for high-temperature filling at 90° or above according to Claims 1 or 2,

characterized in that, in manufacturing of a PET resin having the physical properties of intrinsic viscosity of 0.5 to 1.0 and a melting point of 245 to 260°C, a preform is molded at 275 to 295°C, a neck component is subjected to crystallization at 100 to 200°C, heat setting is carried out at 160 to 200°C, and multistage blowing is carried out at a temperature of 90 to 120°C and a pressure of 20 to 40 kg/cm².